



Europäisches Patentamt
European Patent Office
Office européen des brevets

Publication number:

**0 386 747
A2**

12

EUROPEAN PATENT APPLICATION

21 Application number: 90104378.6

51 Int. Cl.⁵: H01F 1/053

22 Date of filing: 07.03.90

The title of the invention has been amended
(Guidelines for Examination in the EPO, A-III,
7.3).

71 Applicant: **SEIKO INSTRUMENTS INC.**
31-1, Kameido 6-chome Koto-ku
Tokyo 136(JP)

30 Priority: 07.03.89 JP 54497/89

72 Inventor: **Watanabe, Shinji**, c/o Seiko
Instruments Inc.
31-1, Kameido 6-chome
Koto-ku, Tokyo(JP)

43 Date of publication of application:
12.09.90 Bulletin 90/37

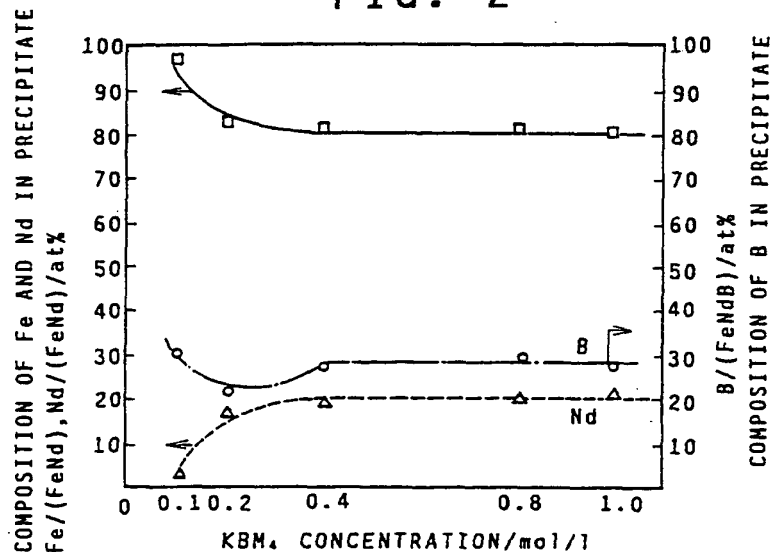
84 Designated Contracting States:
DE FR GB

74 Representative: **Fleuchaus, Leo**, Dipl.-Ing. et al
Melchiorstrasse 42
D-8000 München 71(DE)

54 Method of producing ferromagnetic rare earth-transition metal-boron powder by precipitation.

57 An aqueous solution containing reducing agent such as potassium borohydride or sodium borohydride is added with another solution containing salt of an iron-triads-group element and salt of a rare earth element to conduct reaction to effect reduction to the iron-triads-group metal and the rare earth metal to thereby produce fine powder of rare earth magnet composed of alloy of the iron-triads-group metal and the rare earth metal.

FIG. 2



Xerox Copy Centre

EP 0 386 747 A2

METHOD OF PRODUCING PRECIPITATE OF RARE EARTH FERROMAGNETIC ALLOY

BACKGROUND OF THE INVENTION

The present invention relates to the method of producing fine powder of rare earth magnet.

5 As the conventional method of producing rare earth magnet fine powder composed of alloy of iron-triads-group metal and rare earth metal, there have been known a method of making ingot of mother alloy and then crushing the same, or another method of making ribbon of mother alloy by instant quenching of molten alloy and then crushing the same. Further, chemical reaction method of producing alloy powder has been studied by Saita et al. of Tohoku University (Special Working Group in method of making amorphous
10 metalization and application thereof. The ninth regular meeting text, 28); however, the production of rare earth magnet powder has not been reported.

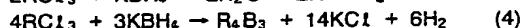
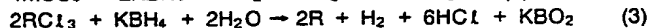
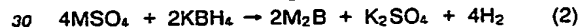
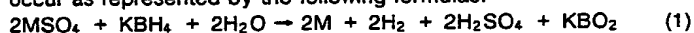
For making and crushing ingot or for making ribbon by instant quenching of molten alloy and crushing the same so as to produce fine powder of rare earth magnet, there has been needed high energy consumption, complicated processes and precious equipments such as a big furnace, liquid instant
15 quenching apparatus and crushing machine, thereby causing the problem of high production cost.

SUMMARY OF THE INVENTION

20 An object of the present invention is to therefore produce fine powder of rare earth magnet at reduced production cost.

According to the inventive practically simple method of adding an aqueous solution containing salt of iron-triads-group metal and salt of rare earth metal to another aqueous solution containing reducing agent
25 such as potassium borohydride or sodium borohydride, fine powder of rare earth magnet can be produced, thereby reducing the production cost and simplifying process as compared to the conventional methods.

When reducing aqueous solution of MSO_4 and RCI_3 by potassium borohydride, reactions concurrently occur as represented by the following formulas:



where M: iron-triads-group element (Fe, Ni or Co) and R: rare earth element.

The reactions are theoretically represented by the above formulas, and actually the resulting substance
35 is composed of R-M-B alloy according to eutectoid mechanism in manner similar to electroless plating. These reduction reactions occur instantly to suppress crystal growth to thereby precipitate fine powder of the R-M-B alloy. Therefore, the fine powder of the R-M-B alloy can be produced directly in contrast to the conventional methods in which ingot or ribbon of the alloy is crushed.

40

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a diagram showing relation between reducing agent concentration and yield of precipitate
45 according to the inventive method; Fig. 2 is a diagram showing reducing agent concentration and composition of precipitate according to the inventive method; Fig. 3 is a diagram showing relation between solution composition and precipitate composition according to the inventive method; Fig. 4 is a diagram showing measurement results, by X-ray diffraction device, of microstructure of precipitate according to the inventive method; Fig. 5 is a photograph, taken by scanning electron microscope, of precipitate according to
50 the inventive method; and Fig. 6 is a diagram showing temperature dependence of saturation magnetization of rare earth magnet obtained according to the inventive method.

DETAILED DESCRIPTION OF THE INVENTION

Hereinafter, the description is given for embodiments of the present invention.

Embodiment 1

5 Fine powder of Nd-Fe-B alloy was produced by the following method. Namely, drops of aqueous solution containing FeSO_4 and NdCl_3 were added into aqueous solution of potassium borohydride to effect reduction reaction to precipitate fine powder of Nd-Fe-B alloy. The precipitated substance was filtered by a glass filter, then washed sequentially by distilled water, methanol and acetone, and thereafter dried in
10 vacuum together with the glass filter.

Concentration of reducing agent

15 A 2.0 ml of aqueous solution containing FeSO_4 and NdCl_3 at mole ratio of 8:2 by concentration of 0.2 mol/l was added to 2.0 ml of aqueous solution containing potassium borohydride at different concentrations of 0.2, 0.4, 0.8, 1.6 and 2.0 mol/l to produce fine powder of Nd-Fe-B alloy in order to determine optimum range of the concentration of the reducing agent. Fig. 1 shows the relation between concentration of the reducing agent and yield of the precipitate. As shown in the figure, whole of Nd ions and Fe ions
20 contained in the aqueous solution of FeSO_4 and NdCl_3 was entirely reduced when the concentration of the reducing agent was more than about 0.5 mol/l. This concentration value is about five times as great as the theoretical value calculated according to the chemical reaction formulas.

Fig. 2 shows the relation between the concentration of reducing agent and the composition of precipitate, which was measurement results by plasma luminescence spectroanalyzer. It was found that
25 stable composition of the precipitate was not obtained in lower range of the reducing agent concentration. In view of the above fact and taking in account of degradation of the reducing agent, the concentration should be set eight to twenty times as much as the calculated value for safety.

Composition of precipitate

A 2.0 ml of aqueous solution containing by concentration of 0.2 mol/l FeSO_4 and NdCl_3 at different mole ratios of 8:2, 4:6, 6:4 and 2:8 was added to 2.0 ml of aqueous solution containing potassium borohydride by concentration of 2.0 mol/l to produce fine powder of Nd-Fe-B alloy. The composition of
35 precipitate was measured by the plasma luminescence spectroanalyzer, the results of which is shown in Fig. 3. According to the results, the ratio of Nd and Fe of the precipitate corresponds to that of FeSO_4 and NdCl_3 in the solution. The boron amount in the precipitate increases proportionally to the Nd amount in the precipitate.

Microstructure of precipitate

A 2.0 ml of aqueous solution containing by concentration of 0.2 mol/l FeSO_4 and NdCl_3 at mole ratio of 8:2 was added to 2 ml of aqueous solution containing potassium borohydride by concentration of 2.0
45 mol/l to produce fine powder of Nd-Fe-B alloy. Microstructure of the precipitate was measured by an X-ray diffraction device, the result of which is shown in Fig. 4. In the figure, rising of the graph on left side is due to the glass filter which was utilized to filter the fine powder of Nd-Fe-B alloy. In the X-ray diffraction, any peak indicative of crystal lattice was not detected. Therefore, it was found that Nd-Fe-B alloy has amorphous microstructure.

50

Particle diameter of precipitate

A 2.0 ml of aqueous solution containing by concentration of 0.2 mol/l FeSO_4 and NdCl_3 was added to
55 2ml of solution containing potassium borohydride by concentration of 2.0 mol/l to produce fine powder of Nd-Fe-B alloy. Particle diameter of the precipitate was measured by a scanning electron microscope, the measurement results of which is shown in Fig. 5. The particle diameter is more or less 0.1 μm and is substantially uniform.

In the above described embodiment, the fine powder of Nd-Fe-B alloy was produced such that it has Fe composition in the range of 0-95 at %, Nd composition in the range of 0-95 at % and B composition in the range of 5-65 at %, and it has particle diameter of more or less 0.1 μm .

5

Embodiment 2

Various kinds of neodymium salt and iron salt were utilized as listed in Table 1. A 2.0 ml of aqueous solution containing by concentration of 0.2 mol/l neodymium salt and iron salt at the mole ratio of 8:2 was added to 2.0 ml of aqueous solution containing potassium borohydride by concentration of 2.0 mol/l to produce fine powder of Nd-Fe-B alloy. The obtained fine powder has substantially uniform particle diameter of more or less 0.1 μm , and has amorphous microstructure as confirmed by X-ray diffraction measurement results.

15

Table 1

Neodymium salts	iron salts
NdF ₃ (dissolved into sulfuric acid and then diluted by water)	FeCl ₂ FeCl ₃ FeSO ₄ · nH ₂ O
NdI ₃ Nd ₂ (SO ₄) ₃ · nH ₂ O Nd(NO ₃) ₃ · nH ₂ O Nd ₂ (CH ₃ COO) ₃ · H ₂ O	Fe ₂ (SO ₄) ₃ · nH ₂ O Fe(NO ₃) ₂ · nH ₂ O Fe(NO ₃) ₃ · nH ₂ O FeBr ₂ · nH ₂ O
Nd ₂ O ₃ (dissolved into diluted hydrochloric acid)	FeBr ₃ · nH ₂ O FeI ₂ · nH ₂ O Fe(CH ₃ COO) ₂ · nH ₂ O

30

35

Embodiment 3

Fine powder of R-Fe-B alloy having the composition ratio of rare earth and iron 12.5:87.5 was produced with using various salts of rare earth elements listed in Table 2. The obtained fine powder of R-Fe-B alloy was press-formed under magnetic field, then sintered within argon gas at 1000 °C for one hour and quickly cooled to the room temperature, and thereafter treated by aging process at 600 °C to thereby produce tablet of R-Fe-B alloy magnet. Fig. 6 shows temperature dependence of saturation magnetization of the magnet.

45

50

55

Table 2

5

10

15

Rare earth elements
$NbCl_3 \cdot nH_2O$
$PrCl_3 \cdot nH_2O$
$SmCl_3 \cdot nH_2O$
$YCl_3 \cdot nH_2O$

As described above, according to the present invention, fine powder of rare earth magnet can be easily and industrially produced without crushing ingot or ribbon material.

20

Claims

1. A method of producing ferromagnetic powder comprising the steps of:
preparing a solution containing a reducing agent which has a boron element, an iron-triads-group element
ion, a rare earth element ion; and
precipitating ferromagnetic powder composed of alloy of iron-triads-group metal, rare earth metal and
boron.

2. A method according to claim 1; wherein the reducing agent is selected from potassium borohydride
and sodium borohydride.

3. A method according to claim 1; wherein the rare earth element ion is selected from Nd ion, Pr ion, Sm
ion and Y ion.

35

40

45

50

55

FIG. 1

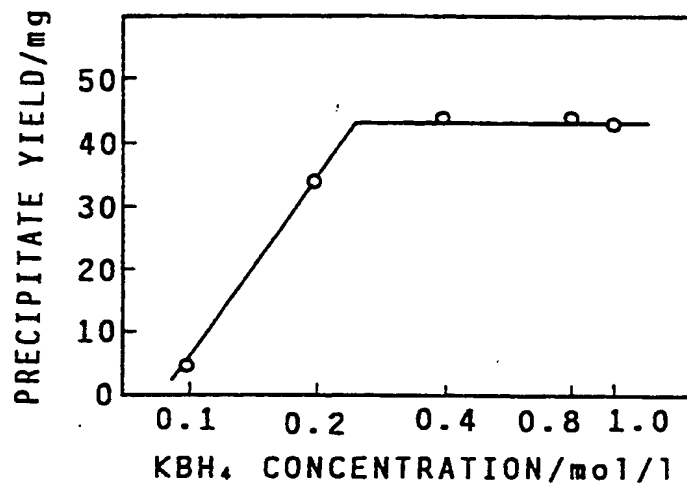
Neu eingereicht. / Newly filed
Nouvellement déposé

FIG. 2

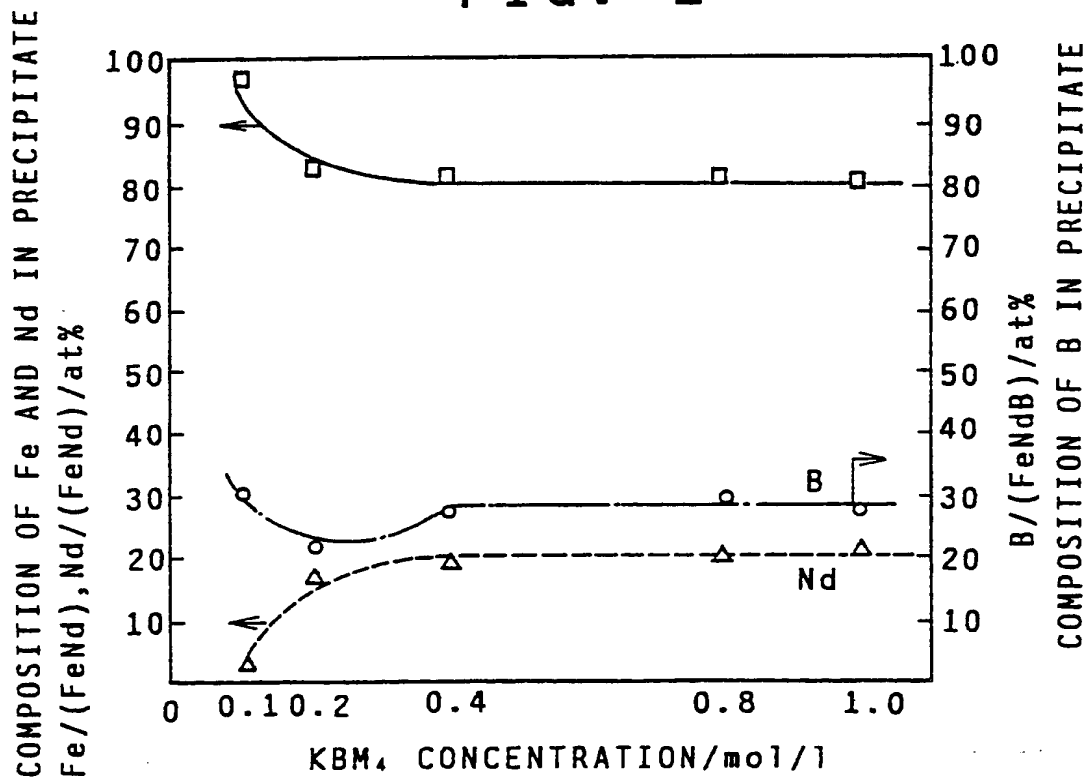


FIG. 3

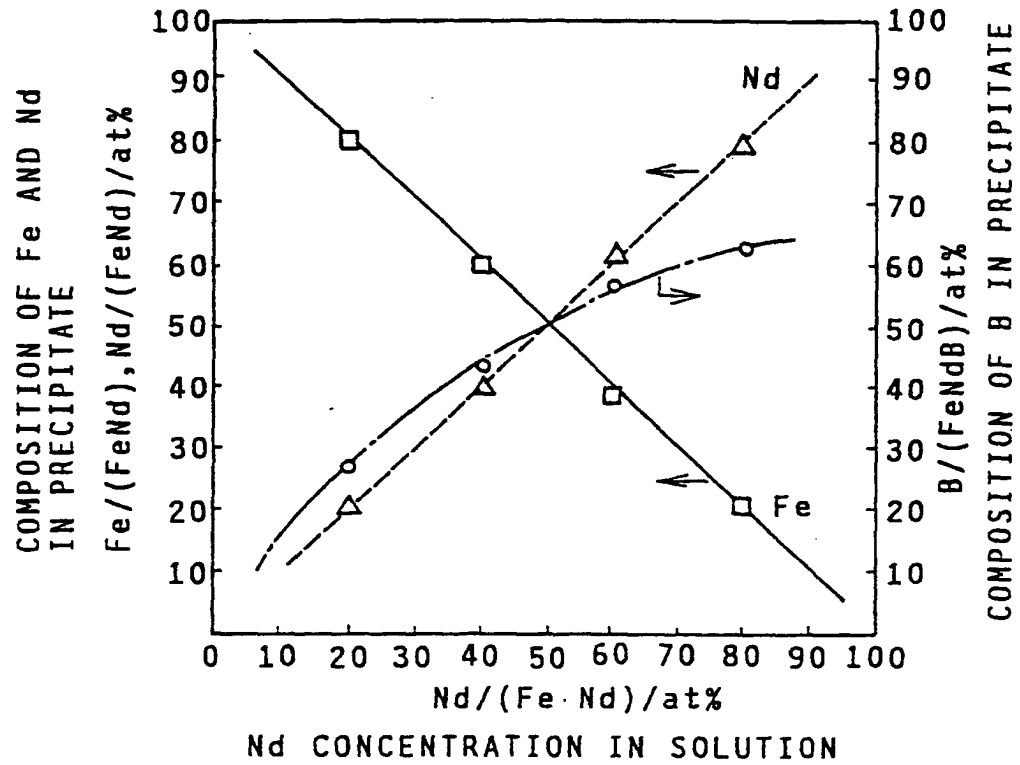


FIG. 4

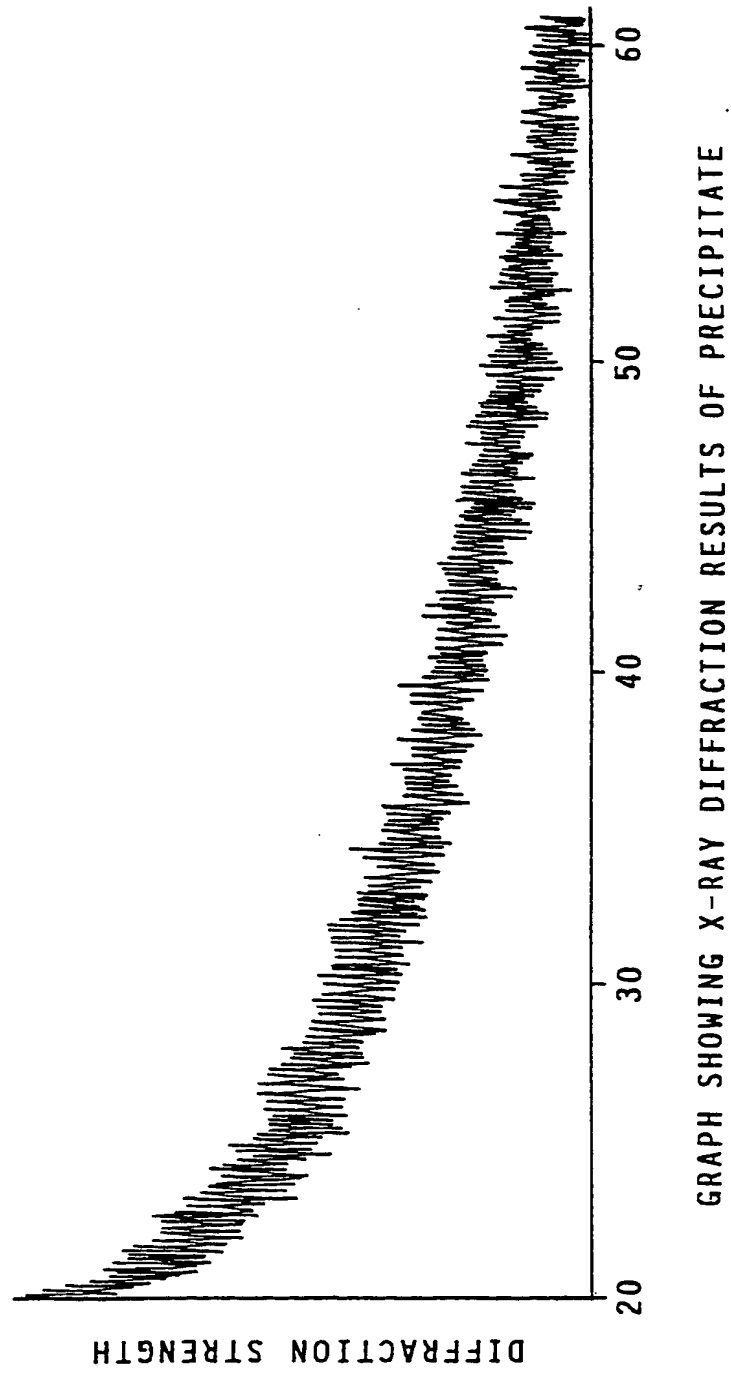


FIG. 5

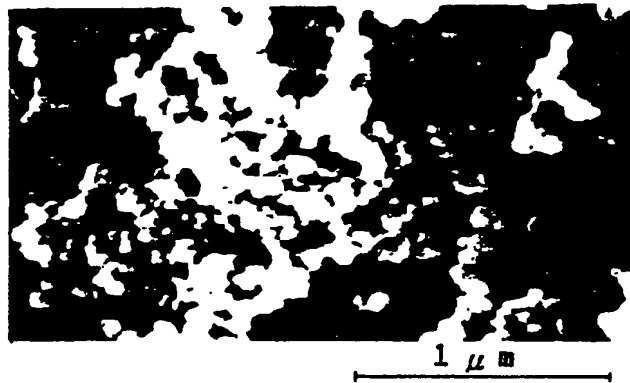
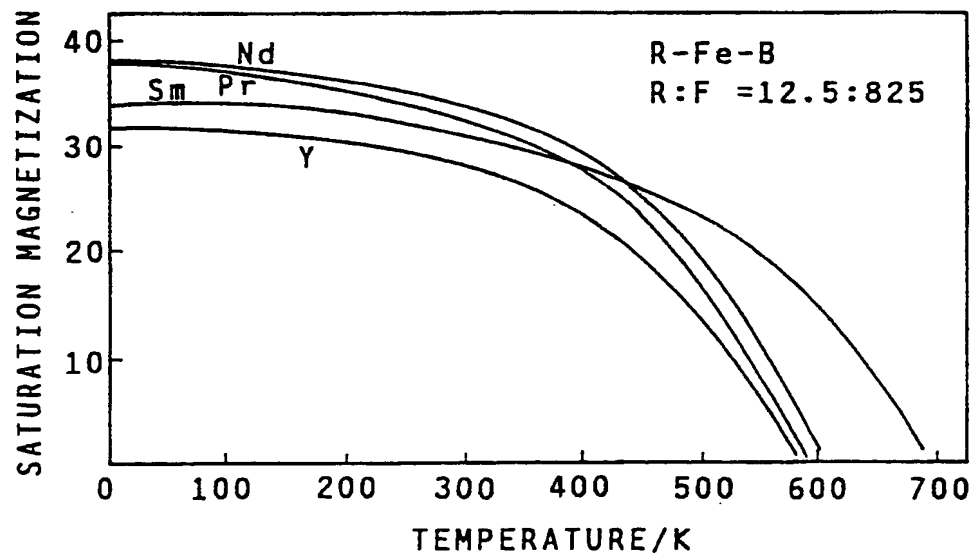


FIG. 6





Europäisches Patentamt
European Patent Office
Office européen des brevets



Publication number: **0 386 747 A3**

12

EUROPEAN PATENT APPLICATION

21 Application number: 90104378.6

61 Int. Cl.⁵: H01F 1/053

22 Date of filing: 07.03.90

30 Priority: 07.03.89 JP 54497/89

43 Date of publication of application:
12.09.90 Bulletin 90/37

94 Designated Contracting States:
DE FR GB

96 Date of deferred publication of the search report:
04.09.91 Bulletin 91/36

71 Applicant: SEIKO INSTRUMENTS INC.
31-1, Kameido 6-chome Koto-ku
Tokyo 136(JP)

72 Inventor: Watanabe, Shinji, c/o Seiko
Instruments Inc.
31-1, Kameido 6-chome
Koto-ku, Tokyo(JP)

74 Representative: Fleuchaus, Leo, Dipl.-Ing. et al
Melchiorstrasse 42
W-8000 München 71(DE)

54 Method of producing ferromagnetic rare earth-transition metal-boron powder by precipitation.

57 An aqueous solution containing reducing agent such as potassium borohydride or sodium borohydride is added with another solution containing salt of an iron-triads-group element and salt of a rare earth element to conduct reaction to effect reduction to the iron-triads-group metal and the rare earth metal to thereby produce fine powder of rare earth magnet composed of alloy of the iron-triads-group metal and the rare earth metal.

EP 0 386 747 A3



European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 10 4378

DOCUMENTS CONSIDERED TO BE RELEVANT					
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)		
X	US-A-4 715 890 (S.R.OVSHINSKY) * claim 1 ** column 9, lines 59 - 63 * - - -	1-3	H 01 F 1/053		
A	US-A-4 394 160 (W.O.FREITAG ET AL.) * claims 1, 4 * - - -	1,2			
E	EP-A-0 370 939 (UNIVERSIDAD DE SANTIAGO DE COM- POSTELLA) * claims 1, 3 * - - - - -	1-3			
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)		
			H 01 F		
The present search report has been drawn up for all claims					
Place of search The Hague		Date of completion of search 09 July 91	Examiner DECANNIERE L.J.		
<table><tr><td>CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention</td><td>E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons ----- &: member of the same patent family, corresponding document</td></tr></table>				CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention	E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons ----- &: member of the same patent family, corresponding document
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention	E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons ----- &: member of the same patent family, corresponding document				